Digest Journal of Nanomaterials and Biostructures Vol. 19, No. 3, July -September 2024, p. 1255 - 1263

Nanoindentation and mechanical characteristics of TiO_2/polypropylene polymer nanocomposite

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This research investigates the nano-titanium oxides (TiO_2), impact on the composition, nano-indenter test, and mechanical characteristics of Polypropylene (PP). The incorporation of TiO_2 nanoparticles into a solution of PP polymer led to the creation of a homogeneous blend. Hydraulic pressing yields a polymer nanocomposite rectangular sheet of 2 millimetres in thickness. In order to examine the nanocomposites, XRD (X-ray diffraction) and FTIR (Fourier transform infrared spectroscopy) were used. The dispersion of the nanoparticles was analysed using a field emission scanning electron microscope (FESEM). The addition of TiO_2 nanoparticles at concentrations of 2 and 4 wt% was used to modify polypropylene, while the proportion of polypropylene remained constant at 1% weight. X-ray and FTIR analysis confirmed the existence of TiO_2, whereas the SEM findings demonstrated the effective distribution of TiO_2 throughout the PP matrix. An investigation was conducted to examine the impact of TiO_2 on the mechanical characteristics of PP. The samples were subjected to mechanical characterizations utilising traditional methods such as flexural strength, tensile strength, impact resistance, and nanoindentation. The mechanical investigation revealed that the nano hardness of the changed coating, as measured by nanoindentation, exhibited a maximum increase of 36.9% in comparison to the unmodified coatings. The nanocomposites exhibited enhanced mechanical characteristics, with the nano hardness and elastic modulus of the nanocomposite samples surpassing those of pure PP.

(Received March 20, 2024; Accepted August 26, 2024)

Keywords: Polypropylene, Titanium oxide, Mechanical properties, Nanoindentation

1. Introduction

Nanocomposites are seen as the forthcoming materials that will bring about a significant industrial revolution. Nanocomposites are a novel category of materials created by using various nanoparticles, including natural, organic, and inorganic elements, as filler substances in distinct polymer mixtures[1], [2]. In recent periods, the main objective has been to discover a composite material of nano-size that is lightweight, environmentally friendly, biodegradable, cost-effective, and suitable for many uses.

Polypropylene (PP) foam offers notable benefits in terms of overall performance, cost of production, and recycling utilisation[3]. Thus, it exhibits more competitiveness in the utilisation of lightweight materials compared to other thermoplastic foams. Nevertheless, general PP is a polymer with a linear and semi-crystalline structure. During the process of foaming, the formation of cells in polypropylene (PP) is naturally uneven due to the inability of the foaming gas to dissolve in the crystalline areas. Furthermore, the poor melt strength of PP may be attributed to its linear chain structure. This phenomenon causes the cell walls of PP to readily merge and break apart when subjected to the stretching strain resulting from cell expansion[4]. The foaming of linear PP is primarily influenced by two issues: low cell density, unequal cell distribution, and a small foaming temperature. These constraints significantly restrict the spectrum of applications for linear PP foaming.

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https://doi.org/10.15251/DJNB.2024.193.1255

Various methods, including incorporating long-chain branching, crosslinking, combining with other polymers, adding particles or fibres, and enhancing foaming processes, have been used to enhance the melt strength and foaming capabilities of PP[5], [6], [7]. Among these options, the use of nanofillers is regarded as a very effective and straightforward method to enhance the polypropylene foaming characteristics. The NPs, when evenly distributed, serve as sites for nucleation(heterogeneous) and tend to lower the energy barrier for nucleation during polymer foaming. This is achieved by causing small fluctuations in stress at a microscopic level in polymer/gas mixtures[8]. As a result, the cell density increases and the dispersion of cell sizes becomes narrower. Titanium dioxide (TiO_2), germanium dioxide (GeO_2), and zinc oxide (ZnO) are semiconductor metal oxide of nanosize that are applied to improve the thermal, mechanical, and chemical resilience of inorganic UV absorbers[9].

This work included the production of a nanocomposite by incorporating TiO_2 nanoparticles into a Polypropylene (PP) matrix at two distinct concentrations. The decision to utilise TiO_2 nanoparticles to improve the coating qualities was informed by a review of existing research. This literature indicated that TiO_2 particles had many advantageous features, including UV stability, strong mechanical capabilities, and effective anticorrosion properties[10], [11]. The impact of TiO_2 nanoparticles on the mechanical characteristics of Polypropylene (PP) is examined.

2. Methods and characterization

2.1. Preparation of samples

The ingredients utilised were polypropylene (PP) and titanium dioxide nanopowder (TiO_2 rutile, with a particle size of less than 100 nm), both of which were bought from Sigma Aldrich. The steps used to make PP and nano TiO_2 polymer nanocomposite materials are as follows. Toluene was used to dissolve polypropylene(isotactic) powder at a temperature of 120^0C. After adding the TiO_2 nanoparticles to the polymer solution and stirring the mixture for two hours, a uniform mixture was achieved. To remove any residual solvent, the samples were vacuum-dried for a full day. A rectangular sheet measuring 2 mm thick is produced by pressing a sample of polymer sheet in a hydraulic press at 160^oC for 8 minutes. This process includes 5 minutes of preheating and 3 minutes at 10 MPa. Prior to removing the sample from the mould, it is chilled at the same pressure.

2.2. Sample characterization

The FT-IR spectra were obtained using the SHIMADZU FTIR 8400S spectrometer, with measurements taken between the wavenumbers of 4000−500 cm^{-1}. The materials were mixed well with KBr. The XRD diffractograms of the TiO_2/polypropylene nanocomposite were analysed using a Rigaku Mini Flex 600s diffractometer at room temperature. This device used an X-ray tube equipped with a copper(anode) to generate radiation (Cu-Kα) at a specific configuration (30 KV). Under SEM (scanning electron microscopy, Jeol JSM-7600 F), the titanium nanoparticles distributed throughout the polymer matrix were studied. Tensile testing was conducted following the ASTM D 638 standard. The dimensions of the composites were 165 mm in length and 19 mm in width. The flexural strengths were examined using ASTM D 790 standards, with a support span of 56 mm and a cross-head speed of 2 mm per minute. Both tests were performed using universal testing equipment and were repeated five times. The impact strength of the material was examined using an INSTRON composite impact tester, following the ASTM D 6110 standard. The test was conducted with ten repetitions.

2.3. Nanoindenter test

Researchers studied the effects of TiO_2 nanoparticle addition on nanomechanical properties, such as elastic modulus and hardness, using a Nano-indenter (Micro Materials, UK) fitted with a Berkovich type indenter. The load control software was used to perform nanoindentation tests with a maximum load of 50 mN. The process started with the sample surface advancing towards the indenter. After the coated surface was detected, the indenter was pushed into the sample at a strain rate of 0.1 mNs^{-1} until the necessary load of 50 mN was obtained. We

assessed the creep behaviour by maintaining the load at its highest level for a duration of 60 seconds. After that, keep draining until the burden is fully gone. An in-built software was utilised to complete all the results analysis. In order to guarantee that the findings were consistent, at least 25 indentations were made in diverse spots.

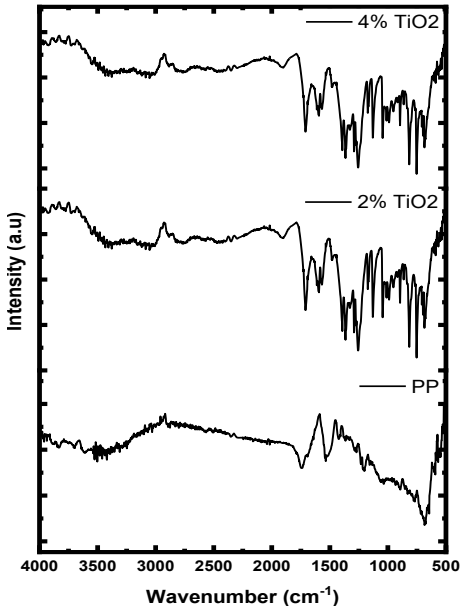

Fig. 1. IR spectra of TiO_2/polypropylene nanocomposite.

3. Result and discussion

3.1. Structure and morphology

Figure 1 displays the FTIR spectra of the TiO_2/polypropylene nanocomposite. The hydrophilicity of TiO_2 nanopowders was shown by the peaks at 1718 cm^{-1} and 3448 cm^{-1} in the PP/TiO_2 absorption spectra. These peaks correlate to the bending and stretching vibrations of the surface -OH groups(hydroxyl). Nanofillers(titanium oxide) in the polypropylene polymer matrix is indicated by the occurrence of a peak at 684 and 752 cm^{-1} in the TiO_2/polypropylene nanocomposite, which is consistent with the characteristics of metal oxides[12].

Figure 2 displays the diffraction patterns of nanocomposites composed of PP with different quantities of titanium nanoparticles included inside their volume. The main peaks at 25.29^0, 37.93^0, and 47.87^0 are indicative of titanium nanoparticles (101), (004), and (200), as shown by the XRD diffraction patterns. In order to catalogue all of the highest points in this particular structure, the ICDD number 21-1272, which corresponds to titanium, may be used[13]. It is evident that a higher concentration of titanium nanoparticles in the polymer leads to a higher degree of crystallinity in the nanocomposites[14]. The relative strength of these peaks in the PP/TiO_2 nanocomposites is directly proportional to the weight percentage of TiO_2 nanoparticles presence. These alterations will impact the physical and mechanical characteristics of PP/TiO_2 nano polymer composites.

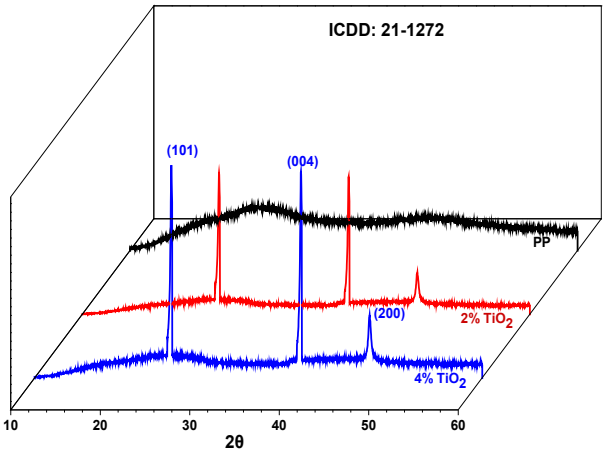

Fig. 2. XRD patterns of TiO_2/polypropylene nanocomposite.

When a strong compatibility is established between the polymer and the filler, it will result in a notable alteration in the structure and form. The usage of Field Emission Scanning Electron Microscopy was employed to validate the distribution of TiO_2 NPs inside PP polymer then it illustrates the resulting morphological alterations. The morphology of the pristine polypropylene (PP) film and PP/TiO_2 nanocomposites with varying TiO_2 NPs concentrations are shown in Figure 3. All the nanocomposites exhibit alterations in the surface morphology compared to pure PP. The visual representation of the well-organized PP material seems uniform and sleek, without any unevenness or coarseness (Fig. 3). Nevertheless, the inclusion of nano-TiO_2 in the PP matrix results in a surface that is both uneven and varied, with the level of unevenness rising as the concentration of TiO_2 in the matrix rises. In addition, the TiO_2 nanoparticles were uniformly distributed without any clumping in the 2% and 4% samples, as seen in Figure 3. The data suggest that the addition of TiO_2 nanoparticles significantly affected the structure of the polymer[15]. This implies that the coupling agent (VTES) interacts with the TiO_2 nanoparticles, stopping them from clustering together. The lone electron pair on the VTES oxygen atom might potentially interact through (Ti^{2+}) in TiO_2 during the compressing and mixing process.

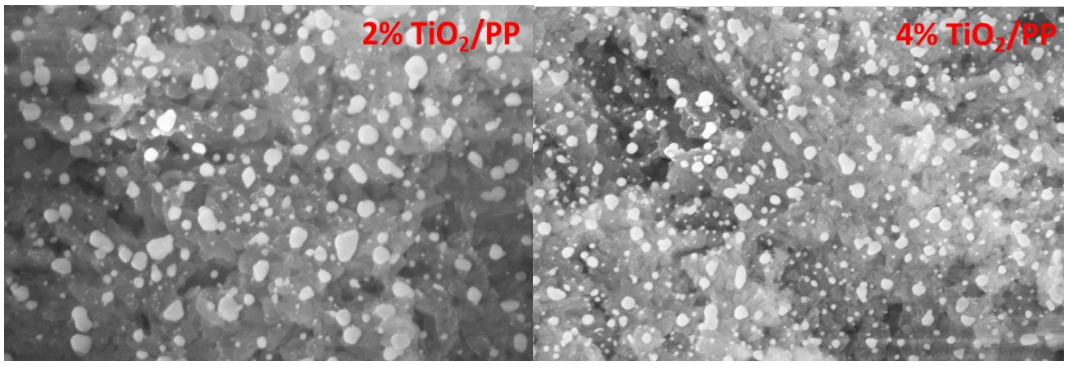

Fig. 3. SEM images of TiO_2/polypropylene nanocomposite.

3.2. Nanoindentation

Figure 4 shows a loading-unloading curve for both PP and nanocomposites with different concentrations. The picture shows that the primary section of the curve (depth around 3800 nm) is a linear segment, indicating the purely elastic response of polypropylene. The subsequent portion of the curve represents the shift from purely elastic to elastoplastic deformation. Table 1 contains the essential parameters acquired from the load-depth relation. The parameters in question are the

depth maximum at peak load, nano-hardness H, and elastic modulus Es. The technique devised by Oliver and Pharr[16] was used to compute the hardness and elastic modulus.

$$H = \frac{P_{max}}{A} \tag{1}$$

where Pmax-peak indentation load and A-projected contact area at maximum load, and

$$E_r = \frac{\sqrt{\pi}}{2}\frac{dP}{dh}\frac{1}{\sqrt{A}} \tag{2}$$

where, Er represents the diminished elastic modulus, which takes into consideration the occurrence of elastic displacement in both the sample and the indenter, and the derivative of P with respect to h is equal to S, where S is the slope of the top section of the unloading curve, which is referred to as the elastic contact stiffness. Therefore, the elastic modulus E of the sample may be determined by:

$$\frac{1}{E_r} = \frac{(1-v_s)^2}{E_s} + \frac{(1-v_i)^2}{E_i} \tag{3}$$

The Poisson's ratio for the sample, denoted as vsi, (0.2 for polymers). The Poisson's ratio for the indenter, denoted as vi, (0.07 for diamond). The elastic modulus for the sample is represented as Es, whereas the elastic modulus for the indenter is denoted as Ei (commonly assumed to be 1141 GPa for diamond). The equation for the elastic modulus of the sample Es may be obtained by rearranging Eq. (3).

$$E_s = \frac{1-(v_s)^2}{\frac{1}{E_r} - \frac{1-(v_{si})^2}{E_i}} \tag{4}$$

Table 1 shows that the average depth maximum at peak load for the pure PP sample is about 8930 nm. In contrast, the nano polymer composites had average maximum depths of 6468 nm and 6174 nm for the 2%TiO_2 and 4%TiO_2 reinforced samples, respectively. The data indicates that the depth at peak load for the 2%TiO_2 and 4%TiO_2 reinforced nanocomposites is about 27% and 31% less than that of the pure PP. The degree of dispersion of nano-TiO_2 may have led to increased resistance to plastic deformation, resulting in a reduced indentation depth[17]. Furthermore, the nanocomposites nano-hardness increased when the TiO_2 level in the samples were raised. Equated to the pure PP sample, the nano-hardness of the 2%TiO_2 and 4%TiO_2 reinforced nanocomposites rose by 28.5% and 30.3% respectively. Specifically, the nano-hardness increased from 0.8640 GPa to 1.209 GPa for the 2%TiO_2 sample, and further increased to 1.241 GPa for the 4%TiO_2 sample.

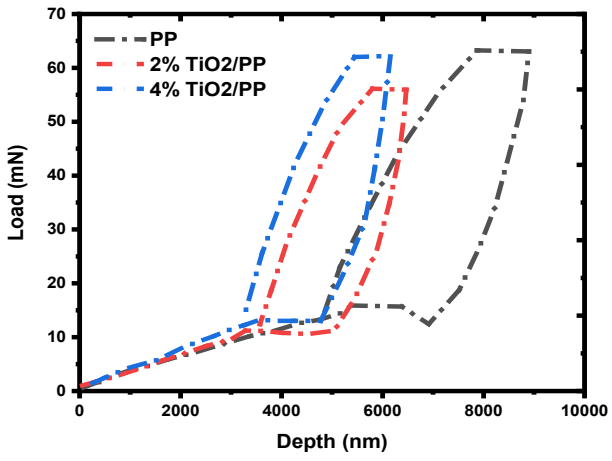

Fig. 4. Nanoindentation of TiO_2/polypropylene nanocomposite.

The Young's modulus(elastic) is a quantity of the strength of the bonds among the atoms. Therefore, it may be changed either by substituting atoms or inserting atoms at the locations of lattice. The Young's modulus is calculated by using the reduced elasticity values as per equation (4). The data shown in Table 1 demonstrates that the elastic modulus of the nanocomposite samples reinforced with 2%TiO_2 and 4%TiO_2 rose by 23.1% and 36.9% respectively, compared to the clean PP. Specifically, the Young's modulus values improved from 0.0528 GPa to 0.0650 GPa for the 2%TiO_2 reinforced sample, and further improved to 0.0723 GPa for the 4%TiO_2 reinforced sample. The modulus and nano-hardness measurements are linked to the distribution of TiO_2 nanoparticles inside the PP matrix. The dispersion of both materials, as seen in Figure 4, led to an increase in nanohardness and modulus when compared to pure PP. Adding hydrophilic nanoparticles to polypropylene hydrophobic polymer is anticipated to reduce the Young's modulus, mechanical and tensile strengths. However, incorporating a coupling agent is expected to enhance the NPs and PP compatibility throughout the mixing heat process by altering the interfacial contact between the NPs and PP [18].

Table 1. Nanoindentation parameters of the TiO_2/polypropylene nanocomposite.

Samples	**Nanoindentation**		
	Maximum depth	**Hardness**	**Reduced modulus**
	nm	**GPa**	**GPa**
PP	8930	0.8640	0.0528
2% TiO_2/PP	6468	1.209	0.0650
4% TiO_2/PP	6174	1.241	0.0723

3.3. Mechanical characteristics

Figures 5a and 5b illustrate the bending properties of a TiO_2/polypropylene nanocomposite with varying concentrations of TiO_2 nanoparticles, ranging from 2% to 4%. The flexural moduli and strengths of composites treated with TiO_2 were significantly higher than those of untreated composites. The reason for this phenomenon is that TiO_2, through its expansive surface-active area, assimilated PP chain molecules, resulting in an augmentation of the interfacial strength of PP. The addition of nano-TiO_2, which has characteristics such as hardness and high modulus, resulted in an enhancement of the flexural modulus inclusion[19]. The addition of nano-TiO_2 to composites has been shown to improve the flexural properties of the material[20]. Elevating the concentration of nano-TiO_2 resulted in an enhancement of the material's flexural properties, therefore leading to an augmentation in the compatibility of PP. Due to the smaller size of nanoparticles, they may be easily injected into the PP. Nevertheless, the composites that were dispersed with nano-TiO_2 particles at a concentration of 4% exhibited the most significant enhancement in flexural properties. The enhancement was achieved due to the condensed size of the particles and their very consistent distribution across the sample. The flexural properties of composites showed a significant enhancement after treatment with 2% and 4% nano-TiO_2 particles. Nevertheless, a higher concentration of nanoparticles resulted in a reduction in flexural strength. The reason for this was an overabundance of nano-TiO_2, which hindered the transmission of stress from the PP matrix. As a result, the interfacial strength decreased.

Table 2. Mechanical properties of the TiO_2/polypropylene nanocomposite.

% TiO_2	**Mechanical Properties**			
	Flexural Strength	**Flexural Modulus**	**Tensile Strength**	**Impact Strength**
	MPa	**MPa**	**MPa**	**KJ/m^2**
2	23	1450	6	2.1
4	25	1631	11	2.3

Figure 5d illustrates the tensile characteristics of TiO_2/polypropylene nanocomposite with concentrations of 2% and 4% respectively. The tensile strength grew steadily from 6 MPa to 11 MPa when the loading of nano-TiO_2 particles was increased, despite variations occurring at higher loadings. The aggregation of 2% nano-TiO_2 particles may be to blame for this high level of stress, which may have been induced by the particle's close proximity to one another. On the other hand, the tensile strengths of samples infused with TiO_2 nanoparticles increased the concentration from 2% to 4%. Nano-TiO_2 particles, in particular those loaded at a concentration of 4%, had the highest tensile strength (11 MPa) out of the two composites.

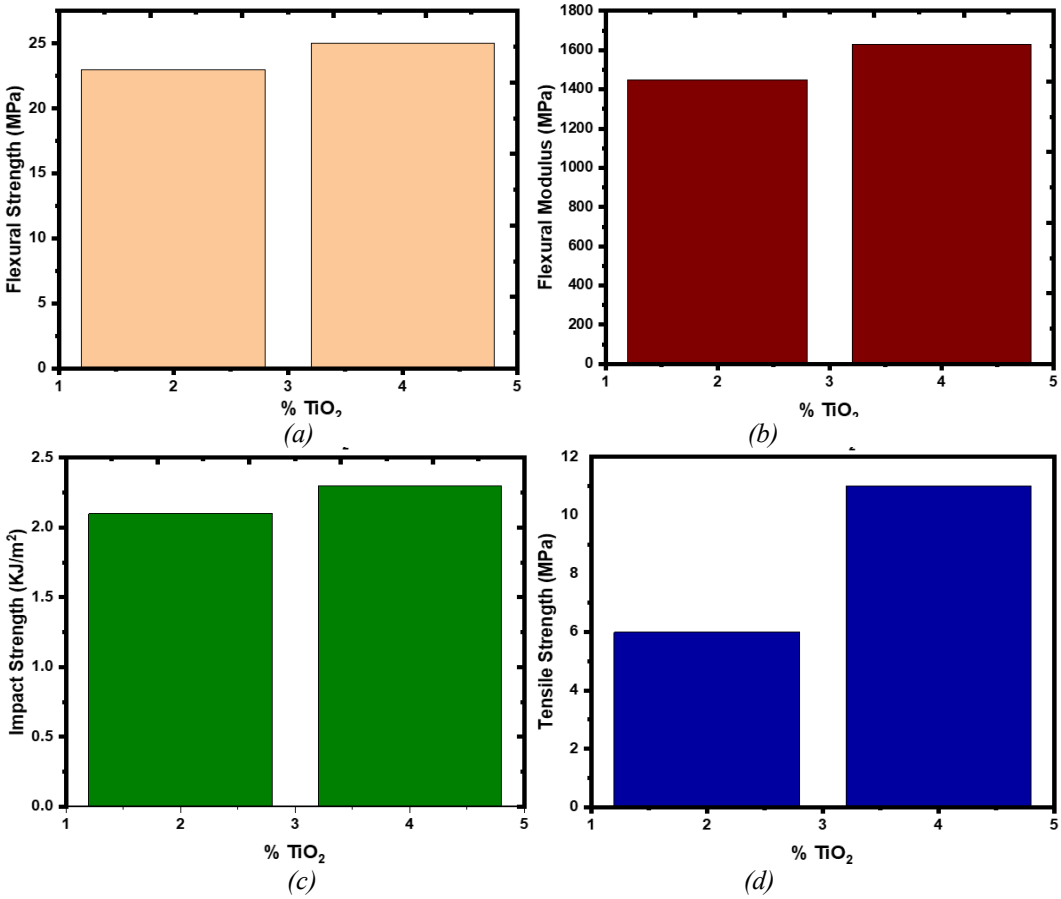

Fig. 5. (a-d) Mechanical characteristics of TiO_2/polypropylene nanocomposite.

This might most likely be ascribed to a greater interlaced intensity that was granted by both a decreased particle size and an enhanced dispersion of nanoparticles. During the tensile testing, there was a significant decrease in the amount of movement of the PP chain. In addition, according to the theory of heterogeneous nucleation[21], the incorporation of nanoparticles into the foam resulted in an increase in the rate at which nucleation occurred. Consequently, a more consistent pore structure has the capacity to enhance the tensile strength of foamed composites. Nevertheless, in other cases, the tensile strength was reduced for specific TiO_2 particle loadings, such as 2%. This discovery suggests that the uniformity of nanoparticles is a critical factor in determining the effectiveness of nano-TiO_2/PP.

Figure 5c depicts the impact strength of TiO_2/polypropylene nanocomposite with 2% and 4% concentrations of TiO_2 nanoparticles. The trends of the impact strength were comparable to those of the flexural (Figure 5a) and tensile (Figure 5d) characteristics. Impact resistance improved from 2% nano-TiO_2 concentrations up to 4%, but then it began to deteriorate beyond those concentrations. It was hypothesised that the drop-in density was caused by fractures brought on by an excessive amount of TiO_2 NPs, it is operated as a irregular phase and energy absorbed during

the impact process. In 4% concentrations of TiO_2 nanoparticles integrated samples showed the highest values of impact strength (2.33 KJ/m^2) when compared to the 2% concentrations.

4. Conclusion

This work aimed to assess the nanomechanical properties and nanoindentation characteristics of polypropylene (PP) by the incorporation of titanium dioxide (TiO_2) nanoparticles. PP/TiO_2 nano polymer composites were synthesised by the solution film forming technique. The incorporated nanoparticles were at varying ratios of 2 and 4 wt%. The existence of TiO_2 was confirmed by FTIR and X-ray analysis. Additionally, the FESEM findings demonstrated that the dispersion of TiO_2 in the PP matrix was satisfactory in samples containing 2 and 4 wt% TiO_2. The mechanical characteristics of the nanocomposites were improved. The nano-hardness of the 2% and 4% TiO_2 nanocomposite samples is greater compared to the pure PP sample. However, the 4% TiO_2 nanocomposite sample has a lower nano-hardness value than the pure PP sample. The impact of incorporating TiO_2 nanoparticles on mechanical properties was assessed by standard mechanical and nanoindentation testing. The morphological analysis revealed that the TiO_2 nanoparticles were uniformly spread and distributed inside the PP matrix, with only a few numbers of visible agglomerations. The dispersion of TiO_2 NPs into the PP matrix resulted in an development in its mechanical strength. The hardness of the unmodified polypropylene increased by 37%, namely from 0.0650 GPa to 0.0723 GPa.

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